

A STUDY OF THE REACTION
BETWEEN NITRIC OXIDE AND
HYDROGEN SULPHIDE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
JERRY ALBERT PIERCE

Baltimore
1928

A STUDY OF THE REACTION
BETWEEN NITRIC OXIDE AND
HYDROGEN SULPHIDE

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
JERRY ALBERT PIERCE

Baltimore
1928

Acknowledgment

The writer is deeply grateful to Doctors W. A. Patrick and J. C. W. Frazer, of the Johns Hopkins University, for having suggested this problem and for their ever-friendly readiness to cooperate. Their advice and encouragement were vitally important in carrying on the work.



A STUDY OF THE REACTION BETWEEN NITRIC OXIDE AND HYDROGEN SULPHIDE*

BY J. A. PIERCE

Introduction

The only direct references to a reaction between hydrogen sulphide and nitric oxide without the aid of an electric spark may be found in two brief sentences in Gmelin-Kraut.¹ Thomson is here quoted as saying that hydrogen sulphide reacts with nitric oxide in a few hours to form a small amount of nitrous oxide and ammonium sulphide. LeConte is credited with replying that they do not react with one another.

In taking up an investigation of a possible reaction between nitric oxide and hydrogen sulphide we had, then, on one hand the contradictory statements of two chemists who labored in what has been aptly called the retort age of chemistry. On the other hand we had the unlimited field of the theories of present day chemistry to draw upon and convince us that such a reaction was theoretically possible. The instability of both nitric oxide and hydrogen sulphide from the thermodynamic point of view was, in itself, sufficient. Previous work in this Laboratory by Hasche and Patrick² on the nitric oxide-oxygen reaction convinced us that there was much potential resemblance between that reaction and the possible one between nitric oxide and hydrogen sulphide.

Our reasons for carrying on this work were, then:

(1) To determine whether or not nitric oxide reacts with hydrogen sulphide, and (a) If it does, to determine qualitatively the resultants of the reaction.

(2) To study the mechanism of the reaction; to determine whether it is an homogeneous gaseous reaction or one affected by the wall of the reaction chamber or by an added catalyst such as silica gel.

(3) Hinshelwood and Green³ believe that, in reactions affecting nitric oxide, two molecules of nitric oxide always enter into the reaction. We wished to test the validity of this theory, and determine, if possible, a general explanation of the mechanism of reactions of this type.

(4) It is known that very few reactions possess a negative temperature coefficient. Practically all of those known have nitric oxide as one of the reactants. We wished to determine whether or not hydrogen sulphide shared with bromine, chlorine, oxygen and hydrogen this same peculiarity.

¹ "Handbuch der anorganischen Chemie," 11, 256 (1907).

² J. Am. Chem. Soc., 47, 1207 (1925).

³ J. Chem. Soc., 1926, 730.

(5) Our preliminary qualitative work showed us quite clearly that the reaction between nitric oxide and hydrogen sulphide was not reversible and, from theoretical aspects, could not be reversible—that it should go to completion. However, we found a rapid drop in the rate of the reaction and a state of equilibrium rather difficult to explain on any grounds other than that of inhibition by one of the resultants. We wished to investigate this as fully as possible.

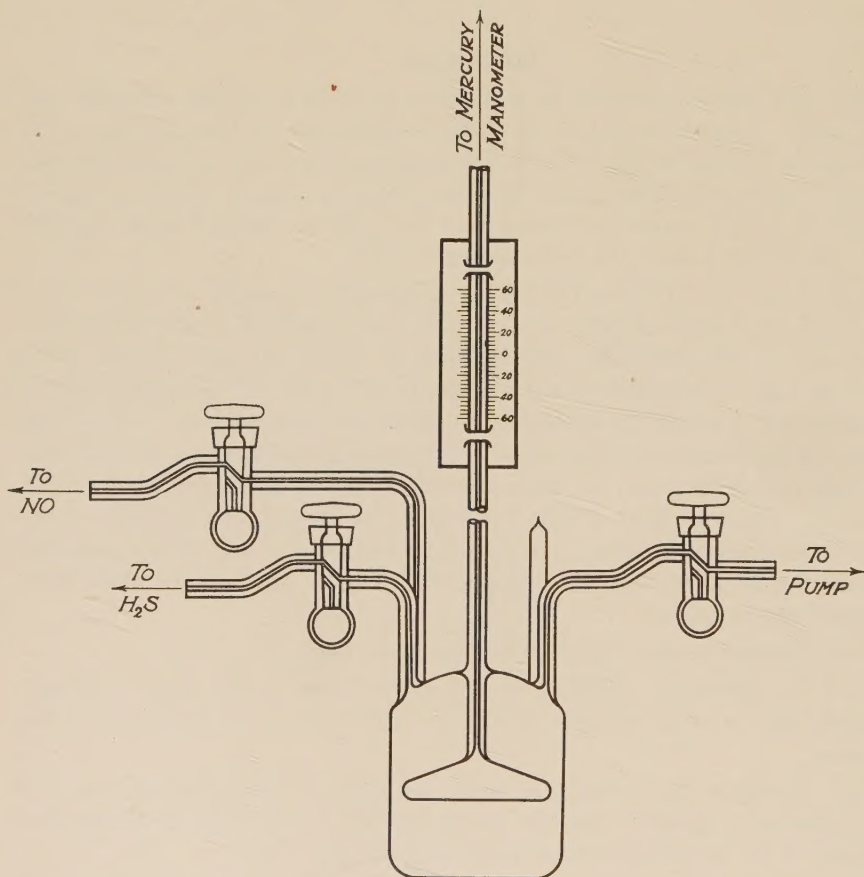


FIG. 1

Apparatus

The essential part of the apparatus used in this work consisted of a modified form of the Klemenc¹ manometer attached to a capillary mercury manometer provided with a leveling bulb. The simplicity of the apparatus eliminated many variables in the carrying on of the work.

Fig. 1 shows in detail the arrangement of the Klemenc manometer as modified by us.

¹ J. Am. Chem. Soc., 47, 2173 (1925).

The funnel-shaped chamber in the interior of the reaction flask has walls of heavy Pyrex, while the bottom is of extremely thin Pyrex. This thin diaphragm is sufficiently thick to endure continual stress, but thin enough to respond instantly to any pressure exerted upon it. It was necessary to make several of these manometers before one was obtained which would give satisfactory results throughout a long period of use. The one finally accepted for the work is sensitive to at least 0.1 millimeter of mercury.

The funnel-shaped chamber has, as its stem, a one-millimeter capillary tube 40 centimeters in length. By evacuating the chamber with its stem under a fluid, and then releasing the pressure, the liquid was brought into the funnel and up the stem to any desired height. This capillary stem was provided with a sliding gauge, the zero point of which was set at the meniscus of the fluid when the reaction chamber was at a pressure of one atmosphere.

The fluid used in our work was alpha-bromonaphthalene fractionated to a constant boiling point and colored purple for greater ease in reading the meniscus. This compound was chosen for its high boiling point, low vapor pressure and low viscosity. Its greatest objection for work of this type is its large coefficient of expansion, which made it necessary for us to have the temperature of the thermostat constant to at least $1/500^{\circ}$ C. However, it offers advantages not to be found in any other fluid we investigated.

Stopcocks used were of the Greiner type. When properly fitted a test extending over a week failed to show gaseous diffusion of any measurable magnitude.

The mercury manometer was of the usual type, open at one arm and provided with a leveling bulb. The bore of the glass tubing used was 2 millimeters, insuring delicacy of reading.

Projecting beyond the stopcocks were three tubes of capillary dimension: one leading to the pump, one to the source of hydrogen sulphide and the third to the source of nitric oxide. The sealed tube shown in the figure and projecting vertically was used for the admission and removal of silica gel and glass wool.

On account of the fact that it was necessary to remove the Klemenc manometer from the rest of the apparatus nearly every day for the purpose of changing the catalyst it was considered inadvisable to have glass-sealed connections between it and the other parts of the apparatus. Only three rubber connections were used, however, and these consisted of short pieces of heavy suction tubing securely wired and completely covered with Duco lacquer.

Evacuation was carried out by means of an oil pump of the most recent design. Experimental use of a mercury pump and a McLeod gauge demonstrated that, no matter how many precautions were taken, hydrogen sulphide gas would penetrate through these pieces and render their accuracy doubtful. Since complete removal of oxygen was of more importance than a high vacuum, it was found that an oil pump alone, with intermittent flushing with oxygen-free nitrogen, was the better usage.

The thermostat consisted of a ten-gallon oil bath fitted with propeller and the usual type of electrically controlled thermoregulator. It was found possible to control the temperature over a reasonable length of time to almost 0.001°C . Variation was rarely greater than 0.05°C , and in such cases the experiment was considered void.

The reaction chamber was immersed in the oil bath until all parts of it were submerged except the stopcocks and the capillary stem.

The Klemenc manometer functioned in the following manner: With atmospheric pressure in the reaction chamber the column of alpha-bromonaphthalene remained—at constant temperature—at a height which may be designated as *A*. The sliding gauge was moved so that its zero point coincided with the meniscus of *A*. Evacuation of the reaction chamber by the pump caused a downward pull on the thin glass diaphragm, and lowered the column of alpha-bromonaphthalene exactly 60 millimeters. (The exact and constant lowering of 60 millimeters throughout the work indicated that the diaphragm had lost none of its original flexibility.) When gas was allowed to enter the chamber the column of fluid ascended to a height proportionate to the amount of gas admitted. The pressure of this gas could be measured by moving the leveling bulb and forcing the alpha-bromonaphthalene column back to its original zero point. This balancing pressure, subtracted from the existing barometric pressure, gave the pressure of the gas in millimeters of mercury. This is in accord with the technique of Klemenc.

Exhaustive preliminary experiments were made to determine the direct ratio between pressure and volume as indicated by the rise and fall of the alpha-bromonaphthalene column. These results—plotted—gave a straight line which agreed, within the limits of experimental error, with calculated results. It was thus possible to measure accurately the volume of the gas in the reaction chamber at any time by the pressure exerted upon the diaphragm. To simplify the work and eliminate the necessity of using gas burettes and confining fluids, the measurement of the gases was carried out by determining their partial pressures and calculating the volume from the curve previously mentioned.

In actual experimentation the initial total pressure of the gases was found. As the reaction proceeded and the total volume of the gases diminished, this decreased volume was determined by observing the decreased pressure. A change in pressure of 0.1 millimeter of mercury was easily read.

Materials

Hydrogen sulphide came compressed in cylinders and was 99.73% pure, the chief impurities being air and moisture. Oxygen was removed by passing the gas over ferric oxide heated to 100°C , water by passing through phosphorus pentoxide. Moore's¹ recommendations as to the purity of liquid hydrogen sulphide were accepted.

Nitric oxide was made by treating sodium nitrite (C. P.) with dilute sulphuric acid (C. P.) according to the method of W. A. Noyes.² It was

¹ Ind. Eng. Chem., **17**, 1023 (1925).

² J. Am. Chem. Soc., **47**, 2170 (1925).

collected over water and dried by passing it through sulphuric acid. No nitric oxide over three weeks old was ever employed.

Nitrogen, used for flushing out reaction chambers and gas containers, was of commercial grade. Oxygen was removed by passing through several columns of freshly prepared pyrogallol solution.

Aside from treatment with phosphorus pentoxide and sulphuric acid no attempt was made to super-dry the gases.

Silica gel was employed in two forms: one was considered to be chemically pure silicon dioxide and the other to contain one percent of ferric oxide. Both were made by the Patrick process.

Glass wool was of the best grade and was strictly lead-free.

Experimental

Qualitative Part:

A few preliminary qualitative experiments were carried on before attempting quantitative work. There was placed in one section of the tube, (Fig. 2) about one gram of silica gel. The tube C was sealed; the open tube D was connected with an oil pump. The apparatus was immersed in an oil bath at 125° - 150° C for three hours in an evacuated condition. Oxygen-free nitrogen was run into the chamber by slipping a rubber tube over C and breaking the glass tube at a previously scratched point within the rubber. Tube C was again sealed and the chamber once more evacuated with heating. Tube D was then sealed and oxygen-free hydrogen sulphide was run in through C as previously described until a pressure of approximately one atmosphere was obtained. Tube C was then finally sealed. Nitric oxide was run into the

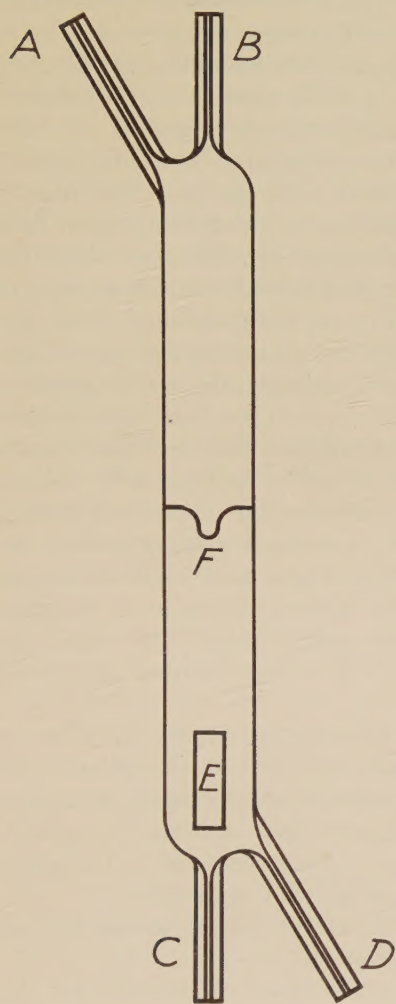


FIG. 2

other section of the chamber through A and allowed to pass out through B for several minutes after all indications of a yellow color had disappeared. Tubes A and B were then sealed, the chamber inverted and the diaphragm broken by the falling of the glass rod *E*. Several of these tubes were prepared. A few were allowed to remain at room temperature for varying lengths of time while others were heated to 195° C for three hours and then put aside.

Quantitative Part:

(A) *In the case where silica gel catalyst was used.* (1) The evacuated reaction chamber of the Klemenc apparatus containing the dried and evacuated gel, and with the gas containers attached was brought to constant temperature. (2) A record was made of, (a) the thermostat temperature, (b) the room temperature, (c) the barometric pressure. (3) The sliding gauge was adjusted so that its 60-millimeter point coincided with the meniscus of the alpha-bromonaphthalene column. (4) Hydrogen sulphide was run in to elevate the alpha-bromonaphthalene column from 60 millimeters to 33.75 millimeters, which represents a volume of 75 cubic centimeters of hydrogen sulphide according to calibration experiments previously described. (5) The hydrogen sulphide was allowed to come to the temperature of the thermostat and to reach a state of adsorption equilibrium with the gel. This usually took about three minutes. (6) Nitric oxide was run in sufficiently to raise the level of the alpha-bromonaphthalene column 26.25 millimeters above the level then existing. (On account of the fact that reaction started the instant nitric oxide began to flow into the chamber it was not possible to obtain the partial pressure of this gas after it had reached the temperature of the thermostat. However, we assumed that, for practical purposes, the partial pressures of the two gases would be of equal value. It required less than three seconds to flow the gases into the chamber.) (7) An immediate reading of the pressure was made with the mercury manometer. (8) Further readings were made at the end of each minute for five minutes, then every five minutes for half an hour, and then every ten minutes until the experiment was concluded. (9) Beckmann thermometer and barometer observations were made at the end of each pressure reading at the termination of the first five minutes. Fluctuations in temperature were watched closely, and, in those cases where the thermoregulator got out of control, the experiment was discontinued and all observations discarded.

Where silica gel was used as catalyst a lowering of pressure was noted as soon as hydrogen sulphide was run in. This is ascribed to adsorption of the gas by the gel in the case of the chemically pure gel, and combined adsorption and reaction in the case of the iron-impregnated gel. A record of such depression was kept. This varied from 0.5 to 5.0 millimeters of alpha-bromonaphthalene according to the form of the gel and the temperature.

Fresh gel was used in each experiment and was previously treated by heat and evacuation to remove water and foreign gases.

(B) *In the case where no added catalyst was used.* The technique was the same as described in the preceding section except that the preliminary procedure consisted merely of heating the opened reaction chamber at about 125° C to remove accumulations of sulphur by oxidation, and to evaporate off water. The success of the treatment was probably variable, and led to some lack of uniformity of results.

(C) *In the case where glass wool was used.* The technique was exactly as in the case where no added catalyst was used. Five grams of glass wool was employed, care being taken to prevent its pressing on the diaphragm.

Results

Qualitative:

Experiments with the sealed tubes showed conclusively that a reaction took place between nitric oxide and hydrogen sulphide. This was indicated, (1) by a rise in temperature, (2) condensation of water on cooled surfaces, (3) the gradual formation of a film of sulphur on the walls of the tube and the surface of the catalyst, and (4) a decrease in pressure of the gases.

Experiments with these tubes were made with chemically pure and iron-impregnated silica gel catalysts. In the former case the pure white gel gradually assumed a lemon-yellow color due to incrustations of sulphur; in the latter case the orange-colored gel (blackened by reaction with hydrogen sulphide) slowly regained, to a limited extent, its original color.

The tube, a tip having been broken under water, showed a decrease in the original pressure of one atmosphere. No attempt was made to determine exact measurements of this decrease.

The water which entered the tube was allowed to remain until the soluble contents were believed to have dissolved. Standard tests for ammonium sulphide were negative. It is assumed, therefore, that the results of Thomson, previously cited, are in error, and, as a corollary, the statement of LeConte that the gases do not react, is without foundation.

Tubes left at room temperature for as long as six months and then opened to the air showed evidence of an equilibrium having been attained. This was indicated by the fact that the entrance of oxygen to the mixed gases formed more sulphur. That is, the reaction between nitric oxide and hydrogen sulphide having stopped, the formation of nitrogen peroxide by contact with air caused further reaction with the remaining hydrogen sulphide. Since the reaction between nitrogen peroxide and hydrogen sulphide is more rapid and more readily visible, the proof of unreacting hydrogen sulphide and nitric oxide in the unopened tube was established.

When iron-impregnated silica gel was used as catalyst the black color of the gel, due to reaction with hydrogen sulphide, was destroyed very slowly and very imperfectly in those cases where the tubes were left at room temperature. Tubes heated above the subliming temperature of sulphur, however, had their catalyst content restored almost to the original orange color. This bleaching process could be checked by again cooling the tube. From this we are led to believe that the removal of the sulphur from the surface of the catalyst eliminated the conditions effecting the equilibrium. That this continuation of the reaction at a higher temperature is not due to a positive temperature coefficient will be discussed in the Quantitative Part.

There are only two stoichiometric possibilities involved in a reaction between nitric oxide and hydrogen sulphide: (1) $\text{H}_2\text{S} + 2\text{NO} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + \text{S}$ and (2) $2\text{H}_2\text{S} + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + 2\text{S} + \text{N}_2$. Briner and Meiner¹ state that N_2O is not a product of the thermal decomposition of nitric oxide. This is a direct rebuttal to the statement of Briner and Boubroff² who had

¹ J. Chim. phys., 23, 609 (1926).

² Comp. rend., 156, 288 (1913).

reported thirteen years before that N_2O is a resultant. Thermodynamic concepts also show us, through free energy calculations, that the reaction is more likely to proceed $2\text{H}_2\text{S} + 2\text{NO} \rightarrow 2\text{H}_2\text{O} + 2\text{S} + \text{N}_2$. We have, therefore, accepted this as the basis of the quantitative work.

Quantitative:

Work with the Klemenc manometer confirmed the results obtained qualitatively.

Experimental work in this section was divided into four series as follows:

(A) In which the gases were allowed to react in the chamber containing no added catalyst.

(B) In which 1.5 grams of chemically pure silica gel served as catalyst.

(C) In which 1.5 grams of chemically pure silica gel impregnated with 1 percent of ferric oxide acted as accelerator.

(D) In which the reaction chamber was stuffed with 5 grams of lead-free glass wool.

Experiments in Series (A), (B) and (C) were made at 28° , 38° , 75° and 100° C. In Series (D) work was carried on at 28° and 100° C. A total of forty-six experiments were made—an average of 3.3 duplications. The first ten were rejected as having been made to establish a technique and to give us an opportunity to correct errors in the apparatus before attempting formal work. A few others were discarded on account of obviously faulty temperature control. The others checked well with their duplicates: this statement being subject to further comment under Discussion of Results.

In Series (A) no decrease in the partial pressure of the hydrogen sulphide due to adsorption was observed although it was very noticeable in the other series. In Series (D), where glass wool was used there was a depression within the limits of 0.5 and 0.1 millimeters of alpha-bromonaphthalene. The absence of a similar depression in Series A is thus considered to be comparative, and dependent upon the extent of the surface.

When nitric oxide was admitted to the chamber, already partially filled with hydrogen sulphide, a rise in pressure always occurred in Series (A) and (D), but never in Series (B) and (C). This increased pressure continued for four or five minutes and had variable values between 0.5 and 2.0 centimeters of mercury. This upward tendency of the curve is considered to be the resultant of vapor pressure, heating effect of adsorption and the downward pull of the reaction. For this reason, the first observations of pressure were discarded and the initial pressure, P_0 , was taken as the first steadily decreasing point on the curve. At the termination of these initial variations curves of all series showed a rapid downward inclination for about forty minutes, and then almost abrupt flattening.

An increased rate of reaction in the presence of glass wool as compared with that where no added catalyst was used affirms our previously derived belief of heterogeneous reaction between these gases.

A direct comparison of the rate of reaction at 28° and 100°C shows a negative temperature effect.

Method of Calculation

Mathematical interpretation of the work was not entirely satisfactory. At the first attempt to find an equation to fit the rate of reaction we were confronted with positive evidence of an inhibitor. Calculations were also complicated by inadequate knowledge of the amount of water vapor each catalyst was capable of adsorbing under the existing conditions, and by a doubt as to the exact interpretation of the initial rise in pressure in experiments of Series (A) and (D). We were also badly handicapped by absence of precedents; the literature on inhibition being very vague as to exact methods of calculation.

We investigated at great length the Freundlich equation, the differential form of which is: $dc/dt = kc^{1/n}$. It failed utterly in our case, no matter what value we gave to n . It was evident that inhibition increased as the reaction proceeded.

Working from the equation: $dx/dt = k(a - x)^n - x$, a purely empirical expression was derived which finally gave fair interpretive results. Due to the unwieldy form of the equation in its integrated form when n was greater than unity, we adopted the mirror method of Latshaw¹ of this Laboratory, whereby dx/dt was determined from the tangent to the curve at each point. The integer, x , does not represent the decrease in the pressure of the volume of gas which has reacted at any particular time, but is a derived value. In the reaction $2\text{NO} + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + \text{N}_2 + 2\text{S}$, we have started with four volumes of gas. If the reaction goes to completion we have one volume of nitrogen and two volumes of water vapor—a total of three volumes. If a is given a value of unity, a decrease of three-fourths in the pressure would mean that the reaction is complete, and $(a - x) = 0$. The value of x would be unity: a fractional change being expressed as $4/3 \Delta P/P_0$.

A new set of curves was drawn, plotting this value of x against time in minutes, and determining dx/dt by Latshaw's method. It was then found that the modified expression, in which a represented unity and $x = 4/3 \Delta P/P_0$ had the same defect as the Freundlich equation, and the original on which ours was based; i. e., there was a steady drop in the velocity constant. After considerable experimentation we found that if, in this equation, we substituted p for a and gave to p the observed pressure at the time t , and then divided the final x by some whole number N , fairly good constants were possible. N was found to be a large numeral, usually 25 or 50. Our equation then became: $dx/dt = k(p - x)^n - x/N$. The magnitude of the divisor N is probably a measure of the extent of the inhibition plus a measure of the condition of the reaction chamber at the beginning of the experiment. That is, if sulphur is the inhibitor and its increase in the reaction chamber in one particular experiment over that in some other experiment makes it necessary to increase the divisor, then any sulphur remaining in the reaction chamber

¹ J. Am. Chem. Soc., 47, 793 (1925).

from a previous experiment would require a further increase in the value of the divisor. We did not realize, at the beginning of the work, the negative character of colloidal sulphur. We used reasonable care in oxidizing residual sulphur at the end of each run in preparation for a new experiment, but it is evident from the mathematical results we have obtained that our reaction chamber was not always in a standardized condition. We believe, however,

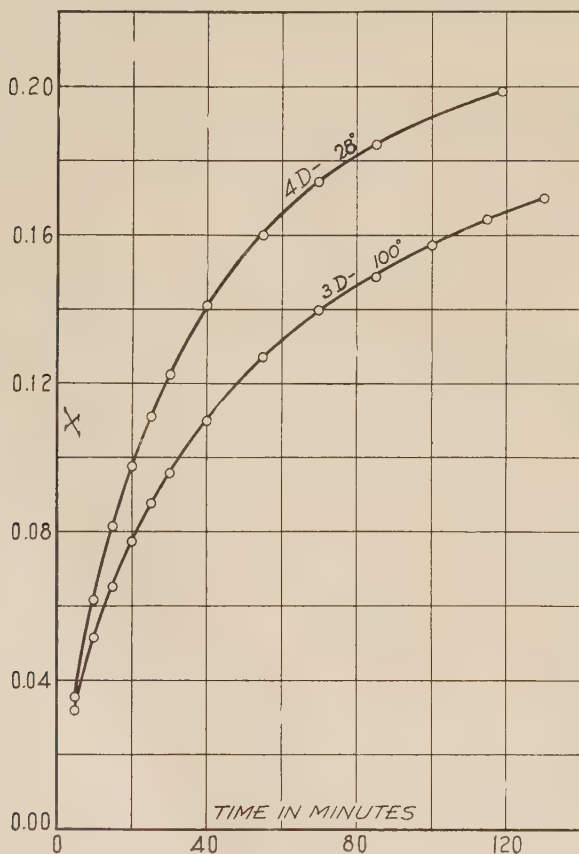


FIG. 3

that, in those cases where the divisor of one final x is equal to the divisor of the final x in another experiment, conditions may be considered as being identical, and on those cases we have determined the character of the temperature coefficient. We obtained particularly good results in Series (D); the experiments of Series (B) and (C) being the most unsatisfactory.

The results of the measurements of two experiments in Series (D) (at 28° and 100° C) are given in Tables I and II, and are shown graphically in Fig. 3.

Temperature Coefficient

$$K_{100}/K_{28} = 0.847$$

TABLE I

Experiment 4-D 28° C; $P_0 = 67.89$ cm Hg; $dx/dt = k(p - x)^3 - x/50$

T (min.)	P	x	$(p - x)^3$	dx/dt	$K \times 10^{-9}$
15	4.15	0.0815	311776	0.00333	159
20	4.99	0.0979	311556	0.00281	153
25	5.67	0.1110	311377	0.00229	145
30	6.24	0.1225	311210	0.00195	141
40	7.19	0.1412	310963	0.00150	139
55	8.17	0.1604	310701	0.00105	137
70	8.89	0.1745	310495	0.00079	138
85	9.39	0.1844	310371	0.00060	138
Mean:					144

TABLE II

Experiment 3-D 100° C; $P_0 = 67.0$ cm Hg; $dx/dt = (p - x)^3 - x/50$

T (min)	P	x	$(p - x)^3$	dx/dt	$K \times 10^{-9}$
10	2.60	0.0517	300063	0.003090	137
15	3.30	0.0653	299888	0.002570	129
20	3.90	0.0776	299714	0.002080	121
25	4.40	0.0875	299579	0.001800	118
30	4.82	0.0959	299472	0.001574	116
40	5.52	0.1099	299284	0.001234	114
55	6.36	0.1270	299056	0.001000	118
70	7.00	0.1393	298895	0.000768	119
85	7.50	0.1488	298761	0.000613	121
100	7.92	0.1576	298640	0.000498	127
Mean:					122

Discussion of Results

The assumption of Thomson that nitric oxide and hydrogen sulphide react to form ammonium sulphide and nitrous oxide is obviously incorrect—absence of the former by qualitative tests being sufficient indication of this. The counter-claim of LeConte that the gases do not react at all is, likewise, refuted. That they do react with formation of water, sulphur and nitrogen is confirmed by our work.

(A) *Mechanism of the Reaction.*

However, the simple stoichiometric equation: $2\text{NO} + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 2\text{S} + \text{N}_2$ does not represent the actual mechanism of the reaction. It is this which we propose to discuss in this section.

Those known reactions in which nitric oxide is a constituent possess peculiarities which have been the subject of much investigation during the

past few years. Work on reactions in which nitric oxide is involved is subject to many difficulties, the chief of which is the necessity of absolute exclusion of air. However, the investigations of recent years have been so uniform in their essential results that there are certain principles which we may accept with confidence. One is the theory of Hinshelwood and Green¹ that in reactions of nitric oxide two molecules of this gas are always involved. Another is that in such reactions as $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$,² $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$,³ $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$ ⁴ and $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ ⁵ there is found either a negative temperature coefficient or a very slight positive one. The extreme rareness and doubtful authenticity of termolecular reactions points to the possibility of intermediate compound formation in all of these. Hasche and Patrick (*loc. cit.*) have demonstrated in their work on the nitric oxide-oxygen reaction the formation of an intermediate of the composition N_2O_3 to account for the apparent third order of their reaction.

We could, with some assurance, postulate in our reaction the formation of an intermediate compound of the composition NOS . In doing so we would be conforming with the results of other investigators in reactions of nitric oxide who have proposed other additive nitrosyl compounds to explain the peculiarities of their results. However, it is quite unnecessary to do this. We prefer to present the theory of selective adsorption.

We have evidence that the reaction takes place on the wall of the chamber and on the surfaces of the catalysts. The condition of the reactants in these adsorbed zones is similar to that found where intermediate compound formation is indicated. That is, forces are brought into play which are similar in their general effect to those present when intermediates are formed. The objection which might be raised against this theory is that we could not, ordinarily, expect nitric oxide to be strongly adsorbed. However, the nitric oxide molecule is strongly reactive and we meet this difficulty by assuming the association of two nitric oxide molecules with the resultant formation of one molecule of N_2O_2 , a supposition supported by Langmuir.⁶

This association of two nitric oxide molecules could reasonably be expected to occur in greater amounts at lower temperatures, and to be incomplete enough at any temperature to escape detection by ordinary density measurements. It would be more easily condensible on the surfaces than the nitric oxide and would, therefore, be adsorbed by the wall in preference to the nitric oxide. The hydrogen sulphide may thus be imagined as impinging on the adsorbed N_2O_2 molecule, and our original stoichiometric equation would become $\text{N}_2\text{O}_2 + 2\text{H}_2\text{S} \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + 2\text{S}$.

Investigation of the critical temperature of the resultants of this reaction indicate that water and sulphur should, in their turn, be more strongly adsorbed than N_2O_2 . Therefore, the surface is denuded of its N_2O_2 and re-

¹ J. Chem. Soc., 1926, 730.

² J. Am. Chem. Soc., 47, 1207 (1925).

³ Z. anorg. Chem., 88, 283 (1914).

⁴ Z. anorg. Chem., 102, 149 (1918).

⁵ J. Chem. Soc., 1926, 730.

⁶ Taylor, "Treatise on Physical Chemistry", (Dushman) II, 1072.

placed by sulphur in a colloidal form. The extremely high critical temperature of sulphur is the foundation of our belief.

It is axiomatic in colloidal chemistry that like substances are adsorbed most strongly by like substances. We may, accordingly, assert the strong possibility of active adsorption between sulphur and hydrogen sulphide, and expect the surface of the sulphur to be coated with an adsorbed film of hydrogen sulphide in preference to one of any other constituents of the reaction.

We have still to consider why we believe that an adsorbed layer of N_2O_2 will react with hydrogen sulphide in the first stage of the reaction when, apparently, the same gas will not react with N_2O_2 in the latter stage. It is undoubtedly a question of orientation. We have, as we have previously explained, a reaction between N_2O_2 and H_2S with the result that a film of sulphur has been deposited on the surfaces. We now assume a selective preference for hydrogen sulphide and consider a film of this gas to be adsorbed by the sulphur with the sulphur ion of the gas in proximity to the elemental sulphur already deposited on the wall. The hydrogen ion of the gas would, then, be turned toward the interior of the chamber. This would demand reaction of gaseous nitric oxide, or N_2O_2 , not with the hydrogen sulphide molecule as a whole, but with the protruding hydrogen ion. That this cannot possibly take place at the temperature we have employed finds confirmation in the previously cited work of Hinshelwood and Green.

We may, therefore, briefly summarize our proposed mechanism of this reaction as follows:

(1) Incomplete but progressive association of two molecules of NO to form one molecule of N_2O_2 .

(2) Adsorption of N_2O_2 on the surfaces.

(3) Reaction between H_2S and adsorbed N_2O_2 .

(4) Adsorption of sulphur on the surfaces.

(5) Adsorption of H_2S on S with orientation of the hydrogen ion toward the interior of the chamber.

(B) *Inhibitory Effect of Colloidal Sulphur.*

The early indications of an inhibitor in this reaction led us to believe that colloidal sulphur was the responsible agency. Its critical temperature indicated that, of all the constituents of the reaction, it should be most strongly adsorbed. Our work was carried on through a range of temperature from 28° to 100°C , and even at the higher temperature there was no indication of a decided transformation of the colloidal form to the crystalline. For this reason we believe that in all of our experiments we were confronted with identical conditions. That is, as the reaction proceeded, the walls of the chamber, the capillaries of the gel and the filaments of glass wool became coated with an increasingly thick accumulation of colloidal sulphur. We had, simply, a strong protective colloid completely covering our catalyst, which eventually prevented contact of the gases with the accelerator. This is very strong confirmation of the heterogeneous nature of the reaction

for, when this deposit of sulphur has reached the critical depth, the reaction stops. The plane surface of the colloidal sulphur is evidently non-catalytic.

Our explanation for the rapidity of the reaction in the experiments of Series A (plain glass walls), and the subsequent retarding of the velocity when sulphur had accumulated is that we were not dealing with plane glass surfaces even when we added no auxiliary catalyst. The corrosive effect of hydrogen sulphide on the water-soluble glass of the walls resulted in neutralization of the soluble alkalies of the glass, and left behind an efficient amount of amorphous silicon dioxide. We were, then, in all four series of our experiments, employing a silicon dioxide catalyst which became impotent when covered with the non-catalytic and impervious colloidal sulphur.

The formation of colloidal sulphur was not of a flocculent type. Thick accumulations could be pulled from glass surfaces in strips. Their elasticity and evident lack of porosity are proof of the great protection the material afforded the catalytic surfaces imbedded within the material.

Data in regard to the inhibitory effect of colloidal sulphur are not found in the literature. Its effect on the mathematical measurement of the velocity of the reaction between nitric oxide and hydrogen sulphide is disastrous. In view of the theoretical importance of both the reaction and the inhibitor, it is hoped that the writer may be in a position to continue the investigation of both.

Summary

(1) The conditions of the reaction between nitric oxide and hydrogen sulphide have been studied at temperatures between 28° and 100° C. Circumstances were varied by carrying on series of experiments in, (a) a plain glass chamber, (b) with added silica gel, and (c) with added glass wool.

(2) It was found that the reaction proceeded under all of the above conditions; the slowest velocity being where no added catalyst was used. Increased surface through the addition of glass wool accelerated the reaction to a rate comparable with that when silica gel was used. It is therefore assumed that the reaction is heterogeneous. This is confirmed by the slowing of the reaction in the presence of inhibiting colloidal sulphur.

(3) The stoichiometric expression for the reaction is: $2\text{NO} + 2\text{H}_2\text{S} \rightarrow 2\text{H}_2\text{O} + 2\text{S} + \text{N}_2$, but the mechanism is more complex. Two molecules of NO associate to form one molecule of N_2O_2 . Hydrogen sulphide impinges on the adsorbed N_2O_2 with the formation of sulphur, nitrogen and water. Hydrogen sulphide is adsorbed by the colloidal sulphur on the surface and oriented in such a way that its hydrogen ion extends outward from the surface.

(4) A negative temperature coefficient was found. This is ascribed to decreased association of NO to N_2O_2 at the higher temperatures.

(5) The accumulation of colloidal sulphur as a resultant of the reaction is the cause of the inhibitory effect observed. It appears to be merely a mechanical coating of the catalyst, and to have the effect of a non-catalytic plane surface.

(6) It is believed that the glass wall of the reaction chamber and the filaments of glass wool were acted upon by water and hydrogen sulphide with formation of amorphous silicon dioxide, i. e., that the catalytic effect of the added silica gel was duplicated by the formation of this amorphous silica, and that results were merely dependent upon quantity.

*The Johns Hopkins University,
Baltimore, Maryland.
June 11, 1928.*

BIOGRAPHY

The author of this dissertation, Jerry Albert Pierce, was born July 25, 1886 in Leadville, Colorado. His early education was received in the Leadville Public Schools and at the Clarke School, Northampton, Massachusetts. He was graduated from the University of Iowa with the degrees of Bachelor of Arts and Graduate in Pharmacy in 1909. During his senior year he was dispenser in the Iowa State Hospital at Iowa City. Until 1914 he carried on pharmaceutical work in Denver, Colorado. From 1914 to 1921 he was in the cattle business in northwestern Colorado. During this period he also did much writing on sociological subjects. In 1922 he entered the University of Denver, where he received the degree of Master of Science in Chemistry. While at the University of Denver he worked for the Great Western Sugar Company as control chemist and later as research chemist. In the summer of 1923 he did independent research at the suggestion of the Great Western Sugar Company as to the nature of the organic sulphur compounds in beet molasses. In August 1923 he joined the staff of E. R. Squibb and Sons, Brooklyn, N. Y. where he carried on research in pharmaceutical and colloidal chemistry. In the fall of 1926 he entered the graduate chemistry department at the Johns Hopkins University and has been in attendance there continuously since that time.

